

LIQUIDS

Water Comes into its Own

from our Molecular Physics Correspondent

THE structural thermodynamics of water, which in the forty years since the classic paper of Bernal and Fowler (*J. chem. Phys.*, **1**, 515; 1933) has so often been a matter of inspired geometrical guessing, shows recent signs of an important fruition which may bring it, if not to the exalted status of the theory of simple liquids, at least to a state in keeping with its general language and methodology. Two very substantial articles (Weres and Rice, *J. Am. chem. Soc.*, **94**, 8983; 1972; Bell, *J. Phys. C*, **5**, 889; 1972) mark this trend, to which a contributory factor has undoubtedly been the appearance of the first convincing computer simulation of a real water model (Rahman and Stillinger, *J. chem. Phys.*, **55**, 3336; 1971; see also *Nature*, **244**, 256; 1973).

As has been stressed on previous occasions (see *Nature phys. Sci.*, **230**, 74; 1971) the available evidence on the structure and dynamics of water from both "ordinary" measurements (density, viscosity, calorimetry) and more sophisticated probes (infrared spectra, neutron and X-ray scattering, nuclear magnetic resonance, dielectric relaxation) seems at times as confusing in its variety as equivocal in its implications. Moreover, the central feature of any theory of water—the hydrogen-bond—remains lamentably ill-defined and can be expected to be the centre of quantum-chemical controversies for some time to come.

Several particular ingredients have combined to make the new models of Weres and Rice and of Bell particularly effective in the present state of knowledge. One is the recently improved potential of Ben-Naim and Stillinger (*J. chem. Phys.*, **52**, 5531; 1970) which, following an earlier proposal by Bjerrum, treats the H₂O molecule as a tetrahedron of positive and negative charges supported on a repulsive core. Another is the recognition that the lattice-gas model, though somewhat discredited in the theory of simple fluids, comes into its own in the case of water, whose complexity still places it somewhat beyond the reach of the more popular integral-equation methods, such as the Percus-Yevick approach.

Given the original Bernal-Fowler picture of an essentially tetrahedral pattern of H-bond linkages, the appropriate lattice cell for the modelling of short-range order is almost unquestionably the partially-occupied body-centred cubic arrangement characteristic of ice-I, within which the H-bonds can "flip" between a well-defined and limited number of configurations, consistent with the so-called "Pauling rules".

Although other authors have attempted to explain the temperature-dependence of density in terms of competition with the denser ice-II structure, the computer experiments, at least, seem to rule out this possibility for normal temperatures and pressures.

Although both Weres and Rice and Bell share the ice-I lattice as starting point and perform similar analyses of the combinatorial statistics of the water molecules in their lattice positions, their approaches, in fact, diverge considerably. Bell, perhaps closer to the spirit of lattice theories, develops his model in terms of two basic parameters, a "bonding-energy" and a "repulsive energy", while Weres and Rice follow through the implications of the BNS potential in great detail, grafting onto their basic lattice model ever more ingeniously-justified elaborations—a quantum harmonic approximation for librational motions, a dielectric continuum to account for inter-cell perturbations, an empirical expansion coefficient to fix the cell dimension, communal entropy taken as proportional to the fraction of intact H-bonds, and so forth, to mention only a few. Although at times they come dangerously close to obscuring the wood by the trees, the effect, after some twenty pages, remains a fine balance of cunning and insight, and the results, a handful of figures giving the various contributions to enthalpy and entropy at 0° and 100° C, are no anti-climax. Though the Weres-Rice results for H and S are not spectacularly close to experiment, they are, by their own high standards, credible, and, moreover, contain useful subsidiary information, for example as to the importance of quantum contributions to the librational motion. Bell, whose approach is overall somewhat less ambitious, rests content that he is able to predict successfully the density maximum, its disappearance at a supercritical pressure, and the observed minimum in isothermal compressibility.

Taken in isolation, both these attempts to reach quantitative thermodynamic conclusions might seem open to the charge of squeezing too much out of an unpromising and grossly underdetermined physical situation. Both undoubtedly contain an unsatisfactory element of seeming to be "designed" to give the type of results by which the authors set particular store—P-V-T data for Bell, S-H-T data for Weres and Rice; neither seems to offer even the remotest chance of predicting a phase transition without very considerable refinement. Nevertheless, an altogether more promising complexion is given to the problem by the Rahman-Stillinger computer simulations which Rice and Weres have

gone to some lengths to consider.

The "molecular dynamics" approach, though still far short of computing the all-important entropy of the system, nevertheless provides (quite literally) an accurate picture of the short-range order and dynamical correlations which follow from the adoption of a particular potential model. Even with the rather restricted samples so far generated (~400 molecules in the most recent work), it now seems clear that several of the wilder guesses as to the nature of the short-range order can be ruled out. Thus, although distorted tetrahedral networks of strained H-bonds are a dominant motif, there seem to be no recognizable "clusters" or regions of anomalous density beyond ordinary thermal fluctuations. Furthermore, although the bonding system seems reasonably well-defined and "dangling" H-bonds can be seen, there seems to be no separation into "network" and "interstitial" molecules and no evidence of interpenetrating networks of the ice-VII and ice-VIII such as required by some alternative lattice-type theories (see, for example, Perram, *Mol. Phys.*, **21**, 1077; 1971). Finally, so far as the dynamics can be interpreted, diffusion seems to occur by strongly coupled motions with no evidence of "jumps" from one relatively long-lived configuration to another. All this undoubtedly adds up to a picture which, at the short-range level at least, is not too far removed from the severely idealized models which Bell and Weres and Rice adopt.

The chief casualty in these findings is, of course, the class of theories whose authors put their faith in the existence of elusive "cooperative effects" in the formation of neighbouring H-bonds, the most picturesque and persuasive of these being the "flickering cluster" model of Frank and Wen (*Discuss. Faraday Soc.*, **24**, 133; 1957). This and other theories involving substantial concentrations on "non-H-bonded" water have already been under fire from infrared spectroscopists (Stephenson, *J. chem. Phys.*, **69**, 2145; 1965), and their passing will surely cause a sigh of relief from theoreticians who, so far from welcoming the simplicity of the appeal to "cooperative effects", see in their radically N-body character something more like a counsel of despair.

Perhaps a large part of the fascination of the water problem lies not so much in its biological importance, or in the judicious rendering of uncertain structural tendencies into soluble mathematics, or in the actual mechanics of what are undeniably tedious calculations—but rather in the exasperating nuances of significance in the process of arriving at what might be called a "best fit" to experimental results drawn from almost every type of physical measurement possible on condensed matter.